Rare Earth-Nickel Hydrides for High-Pressure Hydrogen Storage Materials

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Hydrogen would be ideal as a synthetic fuel, but some problems remain for hydrogen storage. We discussed the possibility of the phase transition between alloy and hydride at high hydrogen pressure from the viewpoint of the hydrogen storage properties in RNi₅-H systems. Between La and Gd in RNi₅-H systems, pressure-composition isotherms show two well-separated pressure plateaux, indicating two kinds of RNis hydrides (β and γ) with one RNi₅ hydrogen solid solution (α). From Tb to Ho in RNi₅-H systems, on the other hand, two pressures disappear gradually, whereas novel plateau appears at low hydrogen content, suggesting the presence of another hydride (β). Due to the lanthanide contraction, the plateau pressures for both α - β and β - γ phase transitions increase with increasing atomic number of R element in RNi₅-H systems in contract to the pressure for α - β ' transitions. Regardless of the RNi₅ composition, the entropy change for α - β transition corresponds to the entropy of H₂ gas while that for β - γ transition is due to the configrational factor of the hydrogen atoms in the unit cell. The plateau pressure depends mainly on the enthalpy due to the constancy of the entropy. The phase transition to form hydride occurs below several GPa at 298 K.

Key words: Hydrogen storage material, Metal hydride, High hydrogen pressure, Phase transition, Plateau pressure

1. INTRODUCTION

Hydrogen would be ideal as a synthetic fuel because it is lightweight, highly abundant and its oxidation product (water) is environmentally benign, but some problems still remain for hydrogen storage as well as hydrogen production [1]. Hydrogen can be stored in three different forms: as compressed hydrogen gas, as liquid hydrogen, as metal hydride.

LaNi₅ is one of the most representative hydrogen storage materials because of its promising hydrogen storage properties at moderate conditions [2]. In a LaNi₅-H system, the pressure-composition (P-C) isotherm shows a single pressure plateau corresponding to the phase transition between LaNi₅ alloy and LaNi₅H_{6.7} hydride.

A plateau pressure is attributed to the unit cell volume of alloy [3], that is, the smaller the unit cell volume is, the higher the plateau pressure is. An increase of hydrogen pressure leads to formation of the plateau. However, P-C isotherms in alloy-H system having high plateau pressure have hardly been clarified yet. Indeed, most of the hydrogen storage properties reported until now have been focused on the plateau pressure within 5 MPa [4]. It is important to understand until how high the hydrogen pressure causes the phase transition.

Recently, we constructed a high-pressure Sieverts' apparatus to measure P-C isotherm at pressures up to 35 MPa [5]. By use of the modified Sieverts' method, we investigated the P-C isotherms in RNi5-H systems (R: from La to Ho) [5-7]. The present study aims to discuss the possibility of the phase transition between alloy and hydride at high hydrogen pressure from the viewpoint of the hydrogen storage properties in RNi5-H systems.

2. EXPERIMENTAL DETAILS

The purity of all starting materials was higher than 99.9% (La, Pr, Nd, Sm and Ni: High Purity Chemicals Co., Ltd., Saitama, Japan; Gd, Tb, Dy and Ho: Santoku Metal Industry Co., Ltd., Kobe, Japan). Binary RNi₅ alloys were prepared by arc-melting under an Ar atmosphere. We confirmed the homogeneity of the samples by means of a scanning electron microscope (SEM) equipped with a wavelength dispersion X-ray spectrometer (WDX). We also identified the crystal structure of the samples using a powder X-ray diffractometer (XRD).

The high-pressure Sieverts' apparatus used in this study has a working pressure range from 0.1 MPa to 35 MPa [5]. Before measurement by the Sieverts' method, the samples were achieved several times under hydrogen at 35 MPa between 196-373 K. The compressibility factor of hydrogen gas (z = PV / RT) was calculated according to the Modified Benedict-Webb-Rubin equation with coefficients provided by the National Institute of Standards and Technology (NIST) [8]. P-C measurements in RNi5-H systems were carried out at least twice with different samples to confirm the reproducibility of the isotherms.

3. RESULTS

3.1 Crystallographic properties

The X-ray powder diffraction profiles for all RNi₅ alloys were assigned to the hexagonal CaCu5-type crystal structure (space group: P6/mmm). Fig.1 shows a schematic representation of the CaCu₅-type structure. R atom occupies the 1a site in the z = 0 plane while Ni atoms occupy the 2c (z = 0) and 3g (z = 0.5) sites.



Fig.1 Hexagonal CaCu₅-type crystal structure of RNi₅ (R: rare earth) alloys with space group P6/mmm.

In the lanthanide series, the electrons successively occupy the inner 4f orbitals, leading to a decrease of atomic radius with an increase in atomic number (Lanthanide contraction). This tendency is retained in the case of their Ni alloys. As reported previously [7], both lattice constants, a and c, of these alloys vary negatively from LaNi₅ to HoNi₅ with keeping c/a ratio, suggesting that the unit cell volume (V) of RNi₅ alloys decreases monotonously as the atomic number of R element increases.

3.2 Pressure-composition isotherm

Fig.2 shows the pressure-composition (P-C) isotherms in RNi₅-H systems at 298 K and 248 K. In light rare



Fig.2 Pressure-composition isotherms on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi₅-H (R: rare earth) systems at 298 K and 248 K.

earth-based RNi₅-H systems (R = Pr, Nd, Sm and Gd), the P-C isotherms show two well-separated plateaux, indicating the presence of two hydrides with compositions of RNi₅H₃₋₄ (β phase) and RNi₅H₆₋₇ (γ phase) together with one RNi5 hydrogen solid solution (α phase). The first pressure plateau corresponds to the α - β phase transition and the second plateau to the β - γ transition. Although the second plateaux for β - γ transition in SmNi5-H and GdNi5-H systems are scarcely distinct at 298 K (a), these systems at 248 K (b) show two unambiguous plateaux. LaNi5-H system has qualitatively similar hydrogen storage properties, in that the plateau pressure of first plateau is in fairly agreement with that of second plateau. This suggests that a single plateau between α and γ phases is present in LaNi₅-H system.

From Tb to Ho in RNi₅-H systems, the first plateau separates and gives rise to another plateau at low hydrogen content. The third plateau indicates an α - β ' phase transition, accompanying the presence of another hydride (β ') with the composition of RNi₅H_{1.5-2.0}. In HoNi₅-H system, the first and second plateaux are no longer distinguishable at any temperature with exception of the third plateau. In the place of appearance of the third plateau, the first plateau as well as the second plateau tend to disappear, leading to drastic decrease of the whole hydrogen content.

3.3 Plateau pressure

The plateau pressures (p_p) determined from the center of each plateau are summarized in Fig.3 as a van't Hoff



Fig.3 van't Hoff plots of plateau pressures on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi_5 -H (R: rare earth) systems.

plot. As mentioned in section 3.1, the unit cell volume decreases with an increase in the atomic number of R element in RNi₅ alloys due to the lanthanide contraction. leading to the size decrease of interstitial sites for hydrogen atoms. Due to the instability of hydrogen, the pressure of first plateau corresponding to the α - β transition increases from the LaNis-H system to GdNis-H system at the same temperature. Similarly, the pressure of second plateau for β - γ transition increases on both hydrogenation and dehydrogenation. However, under these conditions, the pressure becomes undetectable beyond a critical pressure especially on the hydrogenation in the GdNi5-H system and scarcely detectable in the TbNis-H and DyNis-H systems. In contrast to the first and second plateaux, the pressure of third plateau for α - β ' transition decreases with increasing the atomic number of R element.

4. DISCUSSION

4.1 Standard enthalpy change

From the van't Hoff plots of the plateau pressure as shown in Fig.3, standard enthalpy change, ΔH° , and standard entropy change, ΔS° , of phase transitions on hydrogenation and dehydrogenation are calculated as:

$$\ln p_{\rm p} = \Delta H^{\rm o} / RT - \Delta S^{\rm o} / R \tag{1}$$

Here, R is the gas constant and T temperature. These thermodynamic parameters are summarized in Figs.4 and 5. On both hydrogenation and dehydrogenation, the $|\Delta H^{\circ}|$ values for α - β and β - γ transitions decrease with an increase in the atomic number of R element in RNi5-H systems while the $|\Delta H^{\circ}|$ value for α - β ' transition varies inversely, corresponding to the change of the plateau pressure as mentioned in the previous section. As can be seen from Fig. 4, all $|\Delta H^{\circ}|$ values are above 12 kJ mol·H2-1 in any phase transition. For example, the plateau for α - β transition on dehydrogenation in HoNi₅-H system can not be observed on the P-C isotherm as shown in Fig.2, although the $|\Delta H^{\circ}|$ value was predicted from the extrapolation of the α - β transition on dehydrogenation (•) between LaNi5-H and DyNi5-H systems. Similarly the plateau for α - β ' transition (Δ) in GdNi₅-H system is absent. So long as the $|\Delta H^{\circ}|$ value is below 12 kJ mol \cdot H₂⁻¹, the definitive phase transition does not occur practically.



Fig.4 Standard enthalpy changes of phase transitions on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi₅-H (R: rare earth) systems.

The difference of $|\Delta H^{\circ}|$ value between hydrogenation and dehydrogenation, corresponding to the hysteresis, is present for α - β transition, while that for β - γ transition is close to zero, suggesting the small hysteresis. The hysteresis is due to the stress of lattice expansion and contraction during hydrogenation and dehydrogenation. As reported previously [9], the lattice expansion of β - γ phase transition is smaller than that of α - β transition, indicating the small hysteresis. For α - β transition, the difference of $|\Delta H^{\circ}|$ value is somewhat large compared with other two phase transitions, showing large hysteresis on the P-C isotherm in Fig. 2.

4.2 Standard entropy change

The $|\Delta S^{\circ}|$ values for α - β and β - γ transitions on hydrogenation are almost the same as those on dehydrogenation, suggesting the reversible phase transition. In the case of α - β transitions, on the other hand, the $|\Delta S^{\circ}|$ on hydrogenation is somewhat smaller than that of dehydrogenation. This may be due to the phase transition in different pathway between hydrogenation and dehydrogenation like Zr7Ni10-H system [10], in which there are α - γ phase transition on hydrogenation and γ - β and β - α phase transitions on dehydrogenation. The $|\Delta S^{\circ}|$ for α - β transition is about 120 J K^{-1} mol·H₂⁻¹ irrespective of the RNi₅ compositions due to the entropy of H₂ gas. The $|\Delta S^{\circ}|$ for β - γ transition is, on the other hand, is fairly small compared with α - β transition. The difference of entropies between α - β and β -y transitions may be explained by the change in the electronic structure or the configurational term of the hydrogen atoms [11].

For the hexagonal CaCu₅-type unit cell, two possible sites for hydrogen atoms, 3f and 6m, are also shown in Fig. 1 with the metal atom sites. The 3f sites are in the tetrahedral environment situated in the basal z = 0 plane containing R atoms, whereas The tetrahedral 6m sites are situated in the z = 0.5 plane. As neutron diffraction studies by several researchers have shown [12,13], three hydrogen atoms occupy the 3f sites in the initial process of hydrogenation with giving the phase transition of first plateau. Subsequently more three hydrogen atoms occupy the tetrahedral 6m sites on the further hydrogenation, forming the second plateau. This indicates that the occupations by the hydrogen atoms in the 3f and 6m sites correspond to the α - β and β - γ phase



Fig.5 Standard entropy changes of phase transitions on hydrogenation (empty symbols) and dehydrogenation (filled symbols) in RNi₅-H (R: rare earth) systems.

transitions, respectively. From the Boltzmann distribution, the difference of standard entropy changes between these sites are theoretically given as:

$$\Delta S^{\circ} = R \ln \left(\frac{3}{3}\right) - R \ln \left(\frac{6}{3}\right)$$

3*f* site 6*m* site
= ca. -24.5 J K⁻¹ mol·H₂⁻¹ (2)

The calculated value is in fair agreement with the difference of entropies between α - β and β - γ transitions as shown in Fig.5. This suggests that the $|\Delta S^{\circ}|$ values for β - γ transitions is mainly attributed to the configurational factor of hydrogen atoms. Naturally the entropy of H₂ gas decrease with increasing hydrogen pressure [8].

4.3 Upper limit of plateau pressure

According to the van't Hoff equation in Eq.(1), the plateau pressure is related to $|\Delta H^{\circ}|$ and $|\Delta S^{\circ}|$ values: the smaller $|\Delta H^{\circ}|$ value is and/or the larger $|\Delta S^{\circ}|$ value is, the higher plateau pressure is. The $|\Delta S^{\circ}|$ value of the first plateau corresponds to the entropy of H₂ gas (130 J K⁻¹ mol·H₂⁻¹). Due to the constancy of the $|\Delta S^{\circ}|$ value, the plateau pressure depends mainly on the $|\Delta H^{\circ}|$ value. In principle, a phase transition occurs above $|\Delta H^{\circ}| = 0$. In practice, however, the $|\Delta H^{\circ}|$ values determined from the definitive plateaux are above 12 kJ mol·H₂⁻¹ in any phase transition in RNi₅-H systems. In other case, for example, the $|\Delta H^{\circ}|$ value for γ - δ phase transition in LaCo_{4.95}Mn_{0.05}-H system is 14.4 ± 0.7 kJ mol·H₂⁻¹, showing $p_{\rm p} = 106$ MPa at 294 K [14].

The empirical upper limitation of the plateau pressure can be calculated from the thermodynamic values. When the $|\Delta H^{\circ}| = 12$ kJ mol·H₂⁻¹ and $|\Delta S^{\circ}| = 130$ J K⁻¹ mol·H₂⁻¹, the plateau pressure is *ca*. 5 GPa at 298 K, that is, the phase transition to form hydride is scarcely present at higher hydrogen pressure over several GPa.

5. CONCLUSIONS

There are three kinds of phase transitions due to the presence of three RNi₅ hydrides (β , γ and β ') empirically observable in RNi₅-H systems. On the P-C isotherms, the first and second pressure plateaux corresponding to the α - β and β - γ phase transitions separate and their pressures increase with increasing atomic number of R element in RNi₅-H systems from La to Gd. Subsequently, in the TbNi₅-H and DyNi₅-H systems, these plateaux disappear, whereas another third plateau corresponding

to the α - β ^o phase transition appears. Only third plateau is present in HoNi₅-H system. The enthalpy change of the phase transition rather than the entropy change influences the plateau pressure.

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